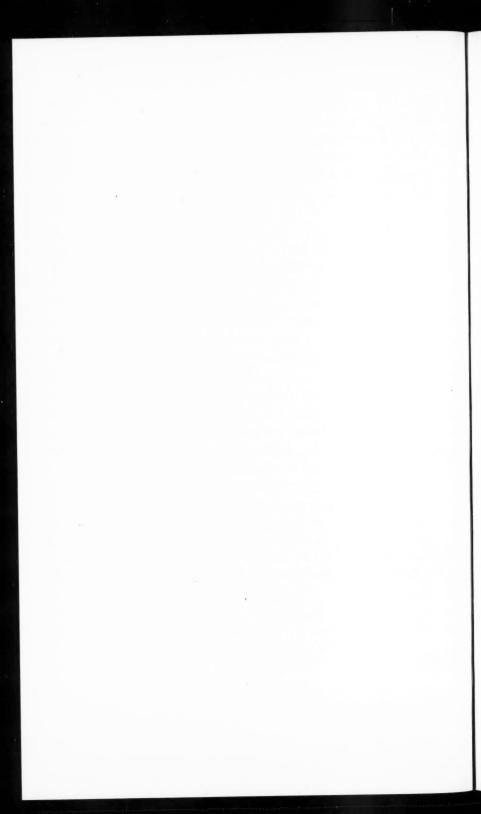
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# EFFECTS OF PRESSURE ON BINARY ALLOYS

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# Effects of Pressure on Binary Alloys

II.

THIRTEEN ALLOY SYSTEMS OF LOW MELTING MONOTROPIC METALS
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### Introduction

This is the second of a projected series of papers on various effects of pressure on binary alloys. The first of the series,¹ published under a title not uniform with that projected for the rest, was on the bismuth-tin and bismuth-cadmium series. In this second paper of the series, alloys of various low melting metals which do not exhibit polymorphism under pressure at room temperature are chosen. The pressure effects on the alloys of such metals are comparatively simple. Studies of alloys of polytropic metals, in particular bismuth and thallium, are reserved for later papers — the phenomena in these systems are much more complex. Low melting metals were chosen for the first investigations because of ease of preparation; other binary alloys of higher melting metals will be studied later.

The effects studied under pressure in this paper are the same as in the first paper of the series, namely: electrical resistance to 30,000 kg/cm<sup>2</sup> at room temperature, electrical resistance to 100,000 kg/cm<sup>2</sup> at room temperature in another apparatus and by a different method, volume compression to 40,000 kg/cm<sup>2</sup>, and plastic shearing strength up to 80,000 and sometimes 100,000 kg/cm<sup>2</sup>. In addition were determined at atmospheric pressure: specific resistance at  $o^{\circ}$ , designated as  $\rho_{00}$ , temperature coefficient of resistance, and density at room temperature. The temperature coefficients were measured between room temperature and o° C, and are given as fractional changes of resistance per degree in terms of resistance at o° C as unity. In all cases a return check reading was made at room temperature, the sequence of readings being: room temperature, o° C, room temperature. The two readings at room temperature were averaged; in most cases there was no difference. This procedure is necessary to avoid error from shifting internal equilibrium or from chemical changes, particularly in those cases where such changes are induced by an exposure to pressure.

The alloys were prepared as before by melting together weighed amounts of the components, usually 2 grams in total amount. The melting was usually done in evacuated pyrex. The molten metals were strongly agitated and rapidly cooled, often by plunging the pyrex tube into a silicone oil. Loss of metal during melting was checked by weighing after casting. Such loss of weight was negligible in almost all cases. Homogeneity of the casting was checked in cases where inhomogeneity was to be suspected by determining the density of the top and bottom halves. Appreciable failures of homogeneity were thus sometimes found; the details will be given under the separate alloys. The alloys containing lithium, calcium, or magnesium were melted in a container of American ingot iron with cover tightly held on with a screw. The alloy was recovered by turning off the container. For these alloys no check was possible on loss of weight.

By far the larger number of the alloys were prepared for the resistance measurements to 30,000 by extruding into wire of 0.020 inch diameter from a steel die. If necessary, the temperature was elevated for the extrusion to sometimes as much as 450°. Certain alloys, however, were too hard and brittle to fashion in this way. Such were pressed into flat plates a few thousandths of an

inch thick between carboloy platens heated to the required temperature. It was often necessary to interpose a thin sheet of mica between carboloy and specimen to prevent sticking, and it was usually necessary to select the specimen with care after pressing in order to avoid cracks. A special method was worked out for measuring the resistance of these specimens. This is the only particular in which the experimental methods of this paper differ from those previously used. After pressing, the thin plate was worked with a razor blade to the shape of a rough rectangular prism approximately 0.240 inch long, 0.040 inch wide, and 0.004 inch thick. This was mounted edgewise in a special holder, and four terminals pressed with springs against the edge. This method has already been applied to certain of the rare earth metals and further details will be found in that paper.<sup>2</sup>

Different sorts of pressure effect are to be expected depending on the nature of the alloy system, whether a homogeneous solid solution, a mechanical mixture, or an intermetallic compound, and the spacing of the compositions studied will be determined accordingly. In general, in the solution range there are specific effects, whereas in the range of mixture the effects are an average of the effects of the components. In the solution range the electrical effects are often large, and a study can be made profitably of dilute solutions in the range of only a few per cent concentration. In the range of dilute solutions it is of interest to find the effect of small amounts of solute on the pressure coefficient of resistance of substances with both positive and negative coefficients. Unfortunately there are not many examples of metals with positive pressure coefficients of resistance which accept appreciable amounts of solute metals. There is a generalization which applies at least to most of the cases hitherto studied to the effect that the addition of a small amount of solute increases the pressure coefficient of resistance algebraically. It will be of interest to find to what extent this generalization applies to the new systems studied here.

Intermetallic compounds may be expected to exhibit specific behaviors not simply connected to that of either pure component. In addition to these points, a further point of interest is to discover other examples of the irreversible formation of new compounds or phases under pressure; one striking example has already been found in the bismuth-tin system.<sup>1</sup> To find the answer to this ques-

tion a single composition, 50-50, will usually suffice for those systems consisting of simple eutectic or having an unlimited solubility range. Another anticipated effect of pressure is a change of the solubility limits. This, however, proved impossibly difficult to investigate at room temperature because of sluggishness of the internal changes.

The metals used in forming the alloys were as follows:

Calcium, "ingot," obtained from MacKay, "better than 99.5%."

Cadmium, "spectroscopically pure," from the New Jersey Zinc Company.

Indium, lump, from MacKay, "99.97% purity."

Lithium, from MacKay, "Na free."

Magnesium, from MacKay, "spectroscopically pure," better than 99.98%, Fe 0.013%, Mn 0.0023%, Pb 0.0013%.

Lead, stock obtained many years ago from the Research Laboratory of the Federated Metals Corporation and used in many of my other measurements. 99.9999% purity.

Antimony, from MacKay, "99.913 pure."

Tin, old Kahlbaum "K" material, purchased shortly after the first world war.

Zinc, "spectroscopically pure," prepared by distillation a number of years ago by the New Jersey Zinc Company.

## DETAILED DATA

There follows now the detailed presentation of data. The order is alphabetical in terms of the chemical symbol. Compositions are in atomic per cents.

Calcium-Cadmium. The phase diagram according to Hansen is complicated, with immiscibility in the liquid phase and presumably at least two intermetallic compounds. Furthermore, large features of the diagram, particularly at the calcium rich end, are in considerable doubt. The system would, therefore, not have been naturally selected for investigation here were it not that Hansen's diagram leaves open the possibility of solubility of cadmium in calcium up to ten per cent or more, and examples of appreciable solubility in a metal with positive pressure coefficient of resistance are rare. Accordingly, three dilute combinations of cadmium with calcium were tried, namely 1, 2, and 5 atomic per cent cadmium. In

addition, the effect of pressure on the resistance of the "pure" calcium from which the alloys were prepared was measured. Except for the compression of the 5 per cent solution and the densities at atmospheric pressure, the measurements were confined to electrical resistance, since it is this that would be expected to be of most significance.

The castings were prepared in an iron crucible with clamped-on lid, which was quenched into water after melting and agitating. The resistance specimens were wires of approximately 0.05 cm diameter, prepared by extrusion from a steel die at 400° to 450° C.

Electrical connections were by spring clips.

The electrical behavior of all the calcium alloys investigated here, including the systems calcium-lead and calcium-magnesium as well as calcium-cadmium, is unlike that of any of the other systems in that there are seasoning effects on the initial application of pressure. The effect of pressure on the fully seasoned cadmium alloys is to increase the resistance at an accelerated rate, the curve of resistance against pressure being concave upward. The seasoning effect was such that on the initial application of pressure, resistance increases at first with downward concavity, which presently reverses with a point of inflection. On first release of pressure at the higher pressures the curve approximately retraces the latter part of the curve on first increase of pressure, but lies below it. Furthermore, the upward concavity persists over the entire pressure range. The net effect is that there is a permanent decrease of resistance after the first application and release of pressure. The same effect was shown also by the "pure" calcium. For this it was shown by special experiment that the seasoning is completed during the first increase of pressure, the curves on subsequent release, reapplication and rerelease retracing themselves. For the several alloys the curves obtained on first release of pressure were accordingly accepted as pertaining to the fully seasoned material, and it is these results which are given in the table. The permanent decreases of resistance after 30,000 kg/cm² for "pure" calcium and 1, 2, and 5 per cent cadmium were respectively 3.7, 2.8, 8.6 and 7.5 per cent.

The results are shown in Table I. The increase of resistance produced by pressure decreases with increasing cadmium content, as would be expected for a simple mechanical mixture, the coefficient of pure calcium being positive and that of cadmium nega-

tive. The curve of resistance against pressure continues concave upward over the range up to 100,000 kg/cm<sup>2</sup> for all compositions.

The resistances now found for "pure" calcium are considerably at variance with those formerly found, the factors of increase

TABLE I
CALCIUM-CADMIUM SYSTEM

	100 Ca	99 Ca 1 Cd	98 Ca 2 Cd	95 Ca 5 Cd	100 Cd
Density	1.533	1.574	1.637	1.750	8.62
Pec × 108	7.46	6.66	5.94	7.32	6.4
Temperature Coefficient Pressure	.00238	.00297	.00288	.00289	.00401
kg/cm <sup>2</sup>			Rp/Ro		
0	1.000	1.000	1.000	000.1	000.1
5,000	1.072	1.065	1.062	1.058	.960
10,000	1.152	1.139	1.130	1.121	.926
15,000	1.223	1.222	1.206	1.194	.897
20,000	1.334	1.312	1.290	1.275	.870
25,000	1.438	1.410	1.384	1.364	.848
30,000	1.567	1.517	1.486	1.461	.828
40,000	1.811		1.705	1.671	.792
50,000	2.069		1.940	1.900	.762
60,000	2.340		2.196	2.087	.736
70,000	2.618		2.460	2.384	.713
80,000	2.916		2.738	2.648	.693
90,000	3.243		3.035	2.930	.675
100,000	3.650		3.380	3.249	.658
			- AV Vo		
5,000				.0268	.0100
10,000	.058			.0497	.0194
15,000				.0697	.0283
20,000	.103			.0886	.0368
25,000				.1063	.0449
30,000	.139			.1220	
35,000				.1360	
40,000	.168			.1481	

under 30,000 and 100,000 respectively now being 1.567 and 3.650 against 1.450 and 4.399 formerly. The change at 30,000 is probably a result of higher purity and a more adequate seasoning procedure in the present material. The considerable revision in the value at 100,000 is due in large part to a better procedure for correcting so as to secure agreement in the 30,000 range. In connection with the former value it was stated: "In all probability the resistance at

the upper part of the range is markedly too high." In any event the correction factor necessary to secure agreement between the two ranges is unusually large for calcium and its alloys. This factor is 1.52 for "pure" calcium, and 1.66 and 1.70 for the 2 and 5 per cent cadmium compositions respectively. This means that the uncertainty in the resistance of these alloys at the upper part of the pressure range is somewhat greater than usual.

The electrical data at atmospheric pressure, specific resistance and temperature coefficient, are not as regular as the pressure effects. Specific resistance decreases with increasing cadmium content to 2 per cent, where there is a minimum. The temperature coefficients

are all materially higher than for the pure metal.

The volume compression of the 5 per cent alloy, the only one measured, is markedly less than that of "pure" calcium. This again is what would be expected, the compression of cadmium being of the order of only one third that of calcium.

The densities at atmospheric pressure increase on the whole regularly with composition, the only exception being that the two per cent composition is slightly high. This again would be expected from the very large difference of density of the pure

components.

The best interpretation of the results is complicated by the effect of the impurity in the "pure" calcium from which the alloys were formed. This impurity, according to the analysis, is of the order of 0.5 per cent. This is sufficient to notably affect the electrical parameters, the specific resistance at o° C and the temperature coefficient being respectively  $7.7 \times 10^{-6}$  and 0.00242, against  $3.43 \times 10^{-6}$  and 0.00457 for the pure material as tabulated in Metals Handbook. The differences are large and in the direction to be expected from dissolved impurity. The specific resistances and temperature coefficients of the three alloys measured here vary somewhat irregularly, but all are of the same order of magnitude as for the "pure" MacKay material. It would seem fairly certain therefore, that calcium does accept dissolved impurity, but in only small amount, probably less than one per cent. The irreversible changes of resistance on the first application of pressure are probably due to a shift in the solubility limits toward lower values. This may be in part a true pressure effect and in part an effect of pressure in narrowing the supersaturation limits incidental to the

cooling of the material from the extrusion temperature. The irregularity of the parameter with composition may perhaps be a geometrical effect arising from irregularity in the distribution of the grains of homogeneous material, an effect which might be

anticipated in wires of as small a diameter as 0.5 mm.

With regard to the question as to the effect of dilute impurities in solution on the pressure coefficients of metals with normally positive pressure coefficient, the evidence can only be suggestive and must wait for a final answer for direct measurements on metal as pure as that listed in Metals Handbook. I have made previous measurements  $^4$  of the pressure coefficient to 12,000 kg/cm² of a calcium of presumptively greater purity than that used here, the temperature coefficient of the former material being 0.00299 against 0.00240 here. The former values for  $R_{\rm p}/R_{\rm o}$  at 5,000 and 10,000 kg/cm² respectively were 1.055 and 1.120, against 1.072 and 1.152 found now. This indicates an algebraic increase of pressure coefficient for addition of slight impurity, a change in the anticipated direction.

Calcium-Magnesium. According to Hansen and Metals Handbook these metals form a single intermetallic compound Ca<sub>3</sub>Mg<sub>4</sub>, and the phase diagram consists of two simple eutectic diagrams side by side: one for the system Ca<sub>3</sub>Mg<sub>4</sub>-Mg, and the other for the system Ca<sub>3</sub>Mg<sub>4</sub>-Ca. The eutectics apparently form with no mutual solubility at either end of the various ranges. In the present work four compositions were investigated: one corresponding to Ca<sub>3</sub>Mg<sub>4</sub>, two equally distributed compositions for the system Ca<sub>3</sub>Mg<sub>4</sub>-Mg, and one very roughly in mid range of the system Ca<sub>3</sub>Mg<sub>4</sub>-Ca. The alloys were prepared in the regular way in an iron mold.

The densities of the pure components differ little, being 1.737 for Mg and 1.53 for Ca. The densities of the alloys are in this range, but are not in accord with what would be expected for eutectic mixtures. The density of the compound Ca<sub>3</sub>Mg<sub>4</sub> is 1.64, about what would be expected for a mechanical mixture of Ca and Mg in the corresponding proportions, but the densities of the mixtures with the compound lie higher than would be expected. No data were obtained bearing on the homogeneity of the castings.

All the alloys are mechanically too brittle to extrude, and they were all prepared for the resistance measurements, both to 30,000 and to 100,000, by squeezing between carboloy platens between

mica at 400°. The measurements to 30,000 were with the four razor blade technique so that the specific resistances may have considerable error. There should be no such error, however, in temperature or pressure coefficients of resistance. In the 30,000 range, where resistances could be measured with increasing and decreasing pressure, there was marked hysteresis between increasing and decreasing pressure on the initial application of pressure except, surprisingly, for the composition 61.9 Ca-38.1 Mg. It was assumed that, as in the case of the calcium-cadmium alloys, the hysteresis for the two compositions containing 28.6 and 42.8 calcium was due to accommodation effects, and accordingly the results shown in Table II are those obtained with decreasing pres-

TABLE II
CALCIUM-MAGNESIUM SYSTEM

	100 Ca	61.9 Ca 38.1 Mg	42.8 Ca 57.2 Mg	28.6 Ca 71.4 Mg	14.3 85.7	Ca Mg	100 Mg
Density	1.533	1.66	1.64	1.70	1.74	+	1.74
$\rho_{00} \times 10^6$	7.46	8.07	15 ±	18±	9.6		4.17
Temperature Coefficient	.00238	.00293	.00269	.00231	.00	310	.00420
Pressure kg/cm <sup>2</sup>			Rp	Ro			
o	1.000	1.000	1.000	1.000	1.00	000	1.0000
5,000	1.072	1.025	1.009	199.	.99	000	-9757
10,000	1.152	1.054	1.018	.985	.98	800	.9533
15,000	1.223	1.086	1.028	.979	.9700	.9889	.9337
20,000	1.334	1.124	1.039	-973	.9600	.9812	.9157
25,000	1.438	1.167	1.053	.970	.97	52	.8996
30,000	1.567	1.215	1.066	.972	.96	75	.8851
40,000	1.811	1.308	1.076	1.005	.95	8	.859
50,000	2.069	1.400	1.088	1.034	.95	2	.837
60,000	2.340	1.490	1.102	1.061	.94	9	.817
70,000	2.618	1.581	1.126	1.086	.94	7	.800
80,000	2.916	1.685	1.134	1.117	.94	.6	.786
90,000	3.243	1.801	1.154	1.150	.94	9	.776
100,000	3.650	1.922	1.175	1.190	.95	6	.767
			- AV	Vo			
5,000		.0235		.0216	.01	95	.0134
10,000	.058	.0435		.0388	.03	53	.0263
15,000		.0605		.0535	.04	89	.0383
20,000	.103	.0768		.0664	.06	20	.0499
25,000		.0922		.0784	.07	39	.0606
30,000	.139	.1067		.0900	.08	54	.0706
35,000		.1192		.1003	.09	55	
40,000	.168	.1298		.1112	.10	52	(180.)

sure. The permanent increase of resistance after the initial application of 30,000 was 4.2 and 1.7 per cent respectively. It is to be noticed that these permanent changes of resistance after the initial application of pressure are in the opposite direction from the calcium-cadmium series. The mechanism of the permanent change must therefore be different. This conclusion is fortified by the fact that there is no permanent change for the composition containing most calcium, where it would be expected to be a maximum if the mechanism were the same. The composition containing 14.3 per cent calcium showed no permanent change of resistance, but between 15,000 and 20,000 there was an anomaly consistent with a sluggish transition running at something over 20,000 with increasing pressure and at something less than 15,000 with decreasing pressure. This is indicated in Table II by two values for resistance at 15,000 and 20,000. It is to be noticed that the change of resistance at this transition has an abnormal direction, resistance increasing with increasing pressure, against the direction of volume change.

The resistances in the range 30,000 to 100,000 are of necessity resistances with increasing pressure. Ordinarily the resistances measured to 100,000 are corrected on the basis of comparison with the results to 30,000. The changes of resistance in the 30,000 range were in general so small, however, that this procedure could be adopted for only one composition, that containing 38.1 per cent Mg. Here a correction factor of 19 per cent was applied over the entire range to secure agreement with the 30,000 series in the common range. No correction was applied to the other three compositions, and the resistances as given in the table contain a break in the tangent at 30,000 which there is every reason to think is an artifact of the method of computation. In the 100,000 range the resistance of the composition containing most Mg decreases smoothly with normal upward curvature, reaching a flat minimum at 80,000. The resistance of the others increases over the entire range with upward curvature. The greater increase at 100,000 for the 28.6 Ca composition as compared with the 42.8 composition may well be due to experimental error.

Taken together, the resistance phenomena are not favorable to the diagram of Hansen; in particular there are no outstanding properties at the composition of the compound.

The compressions are shown in Table II. These alloys are so stiff

mechanically that the use of the indium sheath was required to get good results. This was not discovered until measurements had been made on the compound without the sheath. The results for this showed a very wide friction loop, and since they did not fall in line with the other compositions, have been omitted from the tabulation. The compressions of the three acceptable compositions lie between those of the component metals, and there is no reason to think that the compression of the compound would not also fall into place. The actually measured compression of the compound, that is, the mean with increasing and decreasing pressure, fell out

of line by being too small.

The shearing measurements showed a striking difference between the compound and the three other compositions. Shearing strength of the compound was so high that measurements could not be extended beyond a pressure of 50,000 kg/cm<sup>2</sup>, and even here the carboloy surfaces were badly abraded and had to be refigured. Up to 50,000 shearing slip of the compound is not smooth, but gritty, like a glass. Shearing strength is very closely linear in pressure over the entire range, reaching 7,200 kg/cm<sup>2</sup> at the pressure 50,000. The shearings of the other three compositions, which presumably are mixtures of the compound with one or the other pure metal, were on the other hand perfectly smooth, and were pushed to a pressure of 80,000 kg/cm<sup>2</sup> with no damage to the carboloy. All these compositions show a knee in the plastic strength curve in the general neighborhood of 20,000, followed by a point of inflection and reversal of curvature, the shearing strength rising with upward acceleration at the top pressures. The shearing strength at 80,000 of the 14.3 Ca, 28.6 Ca and 61.9 Ca compositions was respectively: 2,360, 3,300, and 2,300 kg/cm<sup>2</sup>.

Calcium-Lead. The phase diagram is complicated. Both Hansen and Metals Handbook leave open the possibility of appreciable solubility of lead in calcium. Four dilute combinations of lead and calcium, 0.5, 1.0, 2.0 and 5.0 atomic per cent lead, were accordingly tried in the endeavor to throw light on the question of the effect of small additions to a metal with positive pressure coefficient of

resistance.

Except for the densities, only the electrical resistances of these alloys were measured, resistance being sensitive to small additions. The alloys were extruded to wires of 0.015 to 0.022 inch diameter

at 400° C and electrical connections made with spring clips. The same sort of seasoning effects on the initial application of pressure were found as for the calcium-cadmium system, and the explanation is doubtless the same — an effect of the impurities in the "pure" calcium. The resistances with decreasing pressure were retained as final.

The results are shown in Table III. Only two alloys were carried

TABLE III
CALCIUM-LEAD SYSTEM

	100 Ca	99.5 Ca .5 Pb	99 Ca 1 Pb	98 Ca 2 Pb	95 Ca 5 Pb
Density	1.533	1.603	1.622	1.709	1.952
$\rho_{00} \times 10^8$	7.46	5.29	5.44	5.65	5.75
Temperature Coefficient	.00238	.00308	.00284	.00298	.00303
Pressure kg/cm <sup>2</sup>		R	p/Ro		
O	1.000	1.000	1.000	1.000	1.000
5,000	1.072	1.060	1.062	1.059	1.055
10,000	1.152	1.127	1.137	1.127	1.120
15,000	1.223	1.204	1.217	1.207	1.199
20,000	1.334	1.288	1.305	1.293	1.281
25,000	1.438	1.382	1.404	1.385	1.374
30,000	1.567	1.481	1.511	1.488	1.475
40,000	1.811			1.750	1.685
50,000	2.069			2.068	1.905
60,000	2.340			2.426	2.147
70,000	2.618			2.815	2.400
80,000	2.916			3.228	2.662
90,000	3.243			3.692	2.950
100,000	3.650			4.230	3.277

to 100,000, the 2 and 5 per cent lead. The correction factors for securing agreement with the results up to 30,000 were unusually large and materially different for the two alloys, being 2.75 and 1.54 respectively. The precise numerical values above 30,000 given in the table are not to be taken too seriously, particularly for 2 per cent lead. The upward curvature of resistance against pressure over the entire pressure range and for all compositions is the most significant feature of the results. There is no definite evidence of any appreciable solubility of lead in calcium. The higher specific resistance and lower temperature coefficient of the "pure" calcium

compared with the four alloys suggests the possibility that the dissolved lead may have removed some of the impurities originally in solution in the "pure" calcium.

Cadmium-Lead. According to Hansen the system is a simple eutectic mixture of nearly pure components, the solubility of lead in cadmium being less than 0.1 per cent and that of cadmium in lead possibly 1 per cent. The principal interest of the measurements is in a possible new phase under pressure. Only one composition, 50-50 atomic per cent, is necessary to settle this; no new phases were found. The casting was of high homogeneity, there being no appreciable difference of density between top and bottom halves. The mean density was 10.22 against 9.81 expected for the

TABLE IV
CADMIUM-LEAD SYSTEM

	100 Cd	98 Cd 2 Pb	95 Cd 5 Pb	50 Cd 50 Pb	1 Cd 99 Pb	100 Pb
Density	8.62			10.23		11.35
$ ho_{00}  imes 10^{8}$	6.4	6.71	7-37	11.39	19.35	19.13
Temperature Coefficient	.00401	.00409	.00406	.00397	.00402	.00421
Pressure kg/cm <sup>2</sup>			Rp/R	0		
o	1.0000			1.000	1.000	1.0000
5,000	.9606			.961	-935	.9315
10,000	.9268			.930	.878	.8746
15,000	.8974			.875	.830	.8245
20,000	.8720			.840	.787	.7817
25,000	.8488			.809	.749	.7431
30,000	.8284			.781	.715	.7079
40,000	.792			.738		.651
50,000	.762			.702		.606
60,000	.736			.674		-573
70,000	.713			.651		.546
80,000	.693			.631		.524
90,000	.675			.614		.505
100,000	.658			.600		.490
			$-\Delta V/$	Vo		
5,000	.0108			.0104		8110.
10,000	.0201			.0207		.0224
15,000	.0290			.0305		.0323
20,000	.0372			.0395		.0414
25,000	.0449			.0480		.0499
30,000	.0518			.0560		.0579
35,000	.0584			.0633		.0650
40,000	.0640			.0706		.0718

mixture of pure components. The specimen for the resistance measurement to 30,000 was extruded at room temperature.

The numerical results for the compression and change of resistance are given in Table IV. For the most part, after initial irregularities, both resistance and volume change are between those of the pure components, as is to be expected.

The effect of pressure on the resistance of pure lead was redetermined up to 30,000. The results are slightly different and are to be preferred to the old results which were determined assuming a linear relation between pressure and the change of resistance of the manganin gauge. This revision also entails a small revision in the previously published values for lead between 30,000 and 100,000.

The shearing curve shows no noteworthy incident, but rises smoothly, with normal downward curvature to 1,700 kg/cm<sup>2</sup> at 80,000 kg/cm<sup>2</sup>.

In addition to the 50-50 composition three dilute solutions were tried in order to shed light on the question of mutual solubility. At the cadmium rich end, where according to Hansen any solubility of lead is exceedingly small, two compositions were tried: 2 and 5 atomic per cent lead. Only the temperature coefficient of resistance and the specific resistance of these at atmospheric pressure were determined. The specific resistance shows no behavior suggesting mutual solubility. The temperature coefficient of each of the compositions is appreciably higher than that of pure cadmium, being 0.00409 and 0.00406 for 2 and 5 per cent lead respectively against 0.00401 for pure cadmium. If there were true solubility a diminished coefficient would be expected, so that again there is no evidence for appreciable solubility. Whether the rather unusual increase of coefficient found is real or not would require further investigation to settle. At the other end of the series a 1 per cent solution of cadmium in lead was prepared. In addition to the atmospheric data, resistance was measured to 30,000. None of the properties measured differed by any considerable amount from those of pure lead. The effect of pressure in decreasing resistance is slightly less than for pure lead, the specific resistance slightly greater, and the temperature coefficient slightly less. Any solubility of cadmium in lead at room temperature must therefore be exceedingly small.

Cadmium-Tin. The phase diagram given in Metals Handbook differs from that in Hansen in that it shows more detail above 140°, but below 140° there is agreement that the system consists of a mechanical mixture over most of the range, with little and unknown solubilities at the two ends. The primary interest of this investigation was therefore in the possibility of a new high pressure phase. Measurements were made on three compositions: 25, 50, and 75 atomic per cent. No results were obtained inconsistent with a mixed system in this range.

The densities lie approximately on a straight line joining the pure components, the small deviations from linearity being in the direc-

tion of too small densities.

The resistance specimens for measurements to 30,000 of compositions 25 and 75 per cent were extruded at room temperature; the 50-50 composition was extruded at 100°. The results are shown in Table V. The pressure effect on pure tin given in the table differs somewhat from that previously given. A new measurement of resistance to 30,000 was made, giving for the proportional change of resistance at 30,000 0.2275 against 0.2227 formerly. Exact agreement is not to be expected because of the non-isotropy of tin. The two sets of results were averaged in Table V. No change is demanded in previous results for pure tin above 30,000.

Corrections varying from 5 to 22 per cent were applied to the data for the several alloys to reduce the readings to 100,000 to consistency with the 30,000 measurements in the common range

20,000 to 30,000.

In general the effect of pressure on the two pure components is very similar, and the intermediate compositions lie between the extremes. An exception is that the resistance of the 75 Cd-25 Sn composition shows a small but distinct discontinuity with abnormal increase of resistance at 80,000. This is doubtless a transition of some kind. The volume compressions show the same intermediacy as the resistances at the lower pressures, but at 40,000 the compression of the 50-50 composition rises above that of the extremes by an amount considerably beyond experimental error.

The shearing phenomena, unlike resistance or volume, do show a marked pressure episode. This is most marked with the composition 75 Cd-25 Sn, which shows a shallow maximum and minimum with increasing pressure in the general neighborhood of 40,000

TABLE V
CADMIUM-TIN SYSTEM

	100 Cd	75 Cd 25 Sn	50 Cd 50 Sn	25 Cd 75 Sn	100 Sn
Density	8.62	8.23	7.89	7.52	7.29
₽00 × 106	6.4	7.65	8.90	9.92	11.89
Temperature Coefficient	.00401	.00401	.00395	.00411	.00438
Pressure kg/cm <sup>2</sup>			$R_{\mathbf{p}}/R_{0}$		
0	1.0000	1.000	1.000	1.000	1.0000
5,000	.9606	-957	-955	.954	.9505
10,000	.9268	.920	.915	.915	.9077
15,000	.8974	.887	.882	.880	.8695
20,000	.8720	.858	.851	.849	.8344
25,000	.8488	.834	.824	.821	.8031
30,000	.8284	.808	.800	.794	.7749
40,000	.792	-77 I	.761	.752	.724
50,000	.762	.740	.73I	.716	.683
60,000	.736	.714	.705	.686	.647
70,000	.713	.692	.686	.661	.618
80,000	.693	.672 tr	.669	.639	.592
90,000	.675	.665	.654	.619	.569
100,000	.658	.648	.643	.600	.548
		-	- ΔV/Vo		
5,000	.0108	.0102	.0097	.0095	.0099
10,000	.0201	.0196	.0188	1810.	.0184
15,000	.0290	.0284	.0274	.0265	.0265
20,000	.0372	.0365	.0356	.0343	.0342
25,000	.0449	.0444	.0436	.0419	.0417
30,000	.0518	.0516	.0508	.0491	.0488
35,000	.0584	.0583	.0579	.0554	.0548
40,000	.0640	.0644	.0649	.0610	.0610

kg/cm². At the 50-50 composition there is a maximum and minimum, slightly more pronounced, but compressed into a narrower pressure range centering around 30,000. This result was found with two independent set-ups. At 25 Cd-75 Sn a trace of the anomaly remains in a shallow point of inflection centering around 20,000. The two first compositions show a second smaller anomaly in the neighborhood of 80,000. The absolute shearing strengths at 100,000 range from 1,600 to 2,000 kg/cm² with increasing tin content. Here again it would seem that there are shearing transitions not produced by hydrostatic pressure.

Cadmium-Zinc. This according to Hansen and Metals Handbook is a simple eutectic system, the solubility of either component in the other at room temperature being practically nil. Investigation was therefore limited to the single composition, 50-50. There was appreciable inhomogeneity in the casting, density varying from 7.84 to 8.00, against 8.00 calculated for a mixture of the pure components.

The resistance specimen for 30,000 was extruded at room temperature. Both resistance and compression, shown in Table VI, are smooth in pressure, with no episodes. The compressions are intermediate between those of the pure phases, as are also the

TABLE VI CADMIUM-ZINC SYSTEM

	100 Cd	50 Cd	
		50 Zn	100 Zn
Density	8.62	\ 7.84 \ 8.00	7.08
$\rho_{00} \times 10^{8}$	6.4	6.35	5.5
Temperature Coefficient	.00401	.00399	.00408
Pressure kg/cm <sup>2</sup>		Rp/Ro	
О	1.0000	1.000	1.000
5,000	.9606	.963	
10,000	.9268	.931	.937
15,000	.8974	.905	
20,000	.8720	.881	.887
25,000	.8488	.859	
30,000	.8284	.840	.847
40,000	.792	.809	.812
50,000	.762	.785	.783
60,000	.736	.767	.756
70,000	.713	.750	-733
80,000	.693	.736	.713
90,000	.675	.725	.695
100,000	.658	.714	.679
		- \Delta V/Vo	
5,000	.0108	.0096	.0079
10,000	.0201	.0182	.0157
15,000	.0290	.0263	.0229
20,000	.0372	.0343	.0297
25,000	.0449	.0412	.0362
30,000	.0518	.0485	.0424
35,000	.0584	.0552	.0484
40,000	.0640	.0610	.0541

changes of resistance below 50,000. Above 50,000, however,  $\Delta R$ for the alloy is less than for either component. Any precise significance of the results for  $\Delta R$  is obscured by the non-isotropy of the components, especially zinc. The values of specific resistance and temperature coefficient of pure zinc in the table are old values,8 for different stock.

The shearing curve rises smoothly with normal downward curvature to 3,000 kg/cm<sup>2</sup> at a mean pressure of 80,000 kg/cm<sup>2</sup>. Indium-Lead. Hansen's diagram shows this system as one with complete solubiluty of the two pure components in each other. However Davis and Rowe in the 1948 Metals Handbook give a different diagram on the basis of work not yet published in detail. They do not find unlimited solubility, but a third phase in the solid. The alpha phase, which is a solution of beta in lead, ranges up to about 67 atomic per cent indium. The beta phase ranges from 71 to 82 atomic per cent indium, and the gamma phase, solution of beta in indium, ranges from 85 to 100 per cent indium. The range 67 to 71 is a mixture of alpha and beta, and the range 82 to 85 a mixture of beta and gamma.

Three compositions were made for this investigation, 25, 50, and 75 atomic per cent indium, before the work of Davis and Rowe was known to me. The first two should be phase alpha and the third beta. These three compositions will be referred to in the following as the "intermediate" compositions. Later, four dilute alloys, 1, 2, 98 and 99 indium were added, because the wide solubility ranges in this system offer a particularly favorable opportunity for study of the effect of small amounts of solute on pressure coefficient of resistance. Only the electrical properties of the four dilute solutions were measured, and the pressure effects only to 30,000, these measurements being more accurate than those to

100,000.

In addition to the various alloys, various resistance parameters and the compression of pure indium were redetermined, the internal evidence being that the indium now available is materially purer than the former material.9 The pressure decrement of resistance up to 30,000 is now approximately 12 per cent greater than before. No new measurements were made of resistance between 30,000 and 100,000, but the previously found decrements were corrected by 12 per cent. The volume decrements now found agree

within 1 per cent with the previous values; it is general experience that volume compression is insensitive to impurity.

Since the difference between the liquidus and the solidus curves for this system is everywhere small, the tendency to inhomogeneity in the castings should be small, and no evidence for such was found. The densities of the alloys lie smoothly and almost linearly between those of the pure components, as would be the case with a mechanical mixture, indicating no great intensity of the mutual forces between the components, either in the solution or the beta phase. The specific resistance and the temperature coefficient of resistance, on the other hand, have the smooth catenary shape to be expected of solutions, the resistance of the intermediate compositions rising above that of the end members, and the temperature coefficient falling below. There is no suggestion from either of these curves of a third, beta, phase, but the behavior is as might be expected from Hansen's diagram. That is, the electrical behavior of the beta phase is not distinctive.

The specimens for the resistance measurements to 30,000 were formed into wire by extrusion at room temperature. The 100,000 specimens were also formed cold. The results for resistance are given in Table VII. For the three intermediate compositions the corrections for reducing the results to 100,000 to agreement with those to 30,000 are unusually small, indicating rather unusually satisfactory measurements to 100,000. The corrections were respectively 0, minus 6.0, and plus 6.7 per cent for 25, 50, and 75 per cent indium. The proportional pressure effects on the resistance of these three compositions are all nearly the same, and all are distinctly less than that on the pure components, the difference

becoming accentuated at the higher pressures.

The electrical behavior of the four dilute solutions is the expected one. The addition of small amounts of solute, either indium to lead or lead to indium, result in rather sharp increases of specific resistance and decreases of temperature coefficient of resistance. The numerical magnitude of the decrease of resistance brought about by pressure decreases with addition of solute at both ends of the series. That is, the effect of dissolved solute is to increase algebraically the effect of pressure on resistance. This has been found to be the rule in previous measurements. The percentage change of pressure coefficient brought about by addition of dilute

TABLE VII Indium-Lead System

	100 In	99 In 1 Pb	98 In 2 Pb	75 In 25 Pb	50 In 50 Pb	25 In 75 Pb	2 In 98 Pb	1 In 99 Pb	100 P6
Density	7.28	7.32	7.38	8.36	9.33	10.33	11.25	11.32	11.33
$\rho_{00} \times 10^{8}$	7.85	8.51	9.44	23.6	31.5	31.8	21.14	20.12	19.13
Temperature Coefficient	.00478	.00430	.00410	.00184	.00182	.00208	.00372	.00393	.00421
Pressure kg/cm²					$R_{\mathbf{p}}/R_{0}$				
0	1.0000	1.0000	1.0000	1.000	1.000	1.000	1.0000	1.0000	1.0000
5,000	.9329	.9365	.9411	.963	.962	.958	.9366	.9349	.9315
10,000	.8775	.8847	.8904	.930	.927	.921	.8828	.8795	.8746
15,000	.8286	.8371	.8468	.902	.895	.889	.8358	.8310	.8245
20,000	.7860	.7967	.8090	.876	.868	.861	-7953	.7888	.7817
25,000	.7490	.7627	-7747	.853	.846	.836	-7595	.7518	-7431
30,000	.7166	.7309	.7441	.833	.828	.813	.7282	.7172	.7079
40,000	.659			.797	.796	.776			.651
50,000	.610			.773	.77 I	.746			.606
60,000	.565			-749	.752	.722			-573
70,000	.529			-732	-735	.704			.546
80,000	.496			.717	.724	.687			.524
90,000	.465			.704	.712	.672			.505
100,000	.438			.690	.701	.659			.490
					$-\Delta V/Vo$				
5,000	.0127			.0131	.0124	.0116			.0118
10,000	.0238			.0245	.0236	.0222			.0224
15,000	.0341			.0348	.0339	.0322			.0323
20,000	.0439			.0450	.0439	.0419			.0414
25,000	.0532			.0542	.0532	.0509			.0499
30,000	.0621			.0628	.0617	.0592			.0579
35,000	.0708			.0710	.0700	.0669			.0650
40,000	.0788			.0787	.0772	.0743			.0718

solute is not as great as the change in either specific resistance or temperature coefficient. Furthermore, the alteration in pressure effect becomes less at the higher pressures, which means a decreasing curvature of the relation between pressure and resistance with addition of solute.

The compressions of the intermediate compositions are shown in Table VII. The compressions rise from the lead end of the series with increasing content of indium, but drop slightly at the indium end on passing from 75 to 100 per cent indium. In any event, the difference between the compressions of the pure components is small, and there is no striking effect on alloying.

The shearing curves of the intermediate compositions are smooth, with no indication of new high pressure phases, and exhibit a progressive change in character, from slightly concave downward at 25 per cent indium, to slightly concave upward with point of inflection at the middle of the range for 75 per cent. The absolute shearing strengths at 80,000 for 25, 50, and 75 per cent indium were respectively: 1,400, 1,300, and 1,500 kg/cm<sup>2</sup>.

Lithium-Magnesium. According to Metals Handbook the system at room temperature consists of two solid solution ranges separated by a region of mechanical mixture. The alpha phase, same as pure magnesium, runs from 0 to 20 atomic per cent lithium; the region of mechanical mixture runs from 20 to 30 per cent lithium, and the homogeneous beta phase, same as pure lithium, from 30 to 100 lithium. Hansen gives qualitatively the same diagram, the chief difference being a somewhat lower solubility limit for the alpha phase.

21

00

6

5

0

Measurements were made here on nine compositions: 99.5, 99.0, 98.0, 80, 60, 40, 20, 10, and 5 per cent lithium. The three dilute solutions of magnesium were studied especially because there is here a rather unusual opportunity to find the effect of small additions of solute on a metal with positive pressure coefficient of resistance. The only pressure effect measured for these three compositions was the resistance to 30,000. Of the six remaining compositions three are in the homogeneity range of the alpha phase and the other three in the beta range. The simple rule of mixtures would not be expected to apply to any of these.

The alloys were prepared as usual for systems containing lithium by melting in closed iron containers. The castings were presumably fairly homogeneous since no important differences of density were found between different parts of the same casting. Compositions 99.5, 99, and 98 lithium were extruded cold into wire for the resistance measurements. 5 Li was extruded at 400° and 10 Li was rolled cold to thin strip. Both these compositions were annealed at 400° before measurement. The four remaining compositions, 80, 60, 40, and 20 Li, were squeezed into plates and measured by the four razor blade technique. The 80 Li composition was squeezed cold and the others hot.

The specific resistances, plotted against composition, show the expected catenary shape for solutions as contrasted with a linear

TABLE VIII

# LITHIUM-MAGNESIUM SYSTEM

	Ico Li	99.5 Li 0.5 Mg	99 Li r Mg	98 Li 2 Mg	80 Li 20 Mg	bn	60 Li 40 Mg	40 Li 60 Mg	20 Li 80 Mg	re Li 90 Mg	5 Li 95 Mg	roo Mg
ensity	0.536	0.564	0.536	0.538	0.803		1.070	1.335	1.488	1.644	1.699	1.74
90 X 100	41.6	(3)6:11	0.01	10.1	24		23	91	6.11	0.11	5.56	4.17
Coefficient	.00445	.00438	.00437	.00427	98100	36	19100.	.00250	.00252	.00188	.00327	.00420
ressure kg/cm²		-					Rp/Ro	Ro				
0	000'1	1.000	1.000	1.000	1.000	986.	1,000	1,000		000001	000001	1,0000
5,000	1.036	1.040	1.034	1.031	1,00.1	686.	596.	.950		.9823	-9792	.9757
10,000	1.074	1.082	690.1	1.064	1.000	.993	.934	106.		+996.	2196.	.9533
15,000	1.115	1.125	1.106	1.100	1.000	766.	606.	.860		7156.	.9455	.9337
20,000	1.158	1.171	1.145	1.139	1.002	000'1	888	.834		.9382	.9313	7516.
25,000	861.1	1.216	1.186	1.181	1.000	1.005	.871	.817		.9260	7816.	9668.
30,000	1.237	1.263	1.229	1.226	1.010		.860	908.		.9148	1706.	.8851
40,000	1.302				1.026		.833	.785				.859
50,000	1.363				1.043		.810	.770				.837
000,00	1.424				1.062		.788	.757				.817
000,07	1.483				1.081		694.	.747				.800
80,000	1.546				1.102		-754	.738				.786
000,00	819.1				1.124		.741	.730				.776
000,00	1.698				1.148		.730	.724	889.			.767
							10 -	/Vo				
5,000	.0389				.0319	6	.0253	.0193	0810.			.0134
10,000	.0715				.058	6	.0470	.0381	.0344			.0263
15,000	.1005				.083	7	9990.	.0541	0496			.0383
20,000	.1261				.105	0	.0846	.0685	.0630			0460
25,000	17.85				.125	3	4101.	.0822	1920.			9090.
30,000	6891.				.143	9	.1163	9460.	.0883			9020.
35,000	.1872				951.	5	.1295	1057	7860.			
40,000	.2040				.172	8	.1418	9411.	.1085			

relation for mixtures. The densities, on the other hand, are almost linear in the composition. The temperature coefficients of resistance also behave in the expected way, dropping markedly below the pure metals.

Up to 30,000, resistance of the 20 Li-80 Mg composition, shown in Table VIII, drops smoothly with normal curvature and without hysteresis, except for two slight discrepancies at the two lowest pressures on release of pressure, which are probably instrumental. It is unexpected that the decrease of resistance is greater than for pure magnesium. Since the pressure effect on pure lithium is positive it might be expected that admixture of lithium would affect the pressure coefficient in the opposite direction. 40 Li-60 Mg shows a very similar curve, the proportional drop of resistance being very nearly the same as for the 20 Li composition, except that now a slight hysteresis between increasing and decreasing pressure appears between 10,000 and 30,000, amounting at the maximum to about 2 per cent on the initial resistance. This hysteresis was neglected in tabulating the results, which show the mean with increasing and decreasing pressure. The 60 Li-40 Mg composition again gives a smooth decrease of resistance, this time without hysteresis, and again somewhat greater in absolute magnitude than the effect on pure magnesium. The 80 Li-20 Mg composition behaves in a more complicated manner. On the initial application of 5,000 there is a small increase of resistance, then at 10,000 a small drop, from which up to 30,000 resistance increases with accelerated upward curvature. On release, there are important hysteresis effects; a nearly linear drop down to 5,000 followed by a more rapid drop to zero. In the table the values with increasing and decreasing pressure are shown separately.

The three dilute solutions, 0.5, 1.0, and 2.0 Mg, show comparatively little difference from the 100 per cent lithium. Except for the specific resistance of the 0.5 composition, the differences are in the expected direction — increase of specific resistance and decrease of temperature coefficient. It is to be remarked that the specific resistance of the 0.5 composition had unusually large experimental error because of geometrical irregularities introduced by the extrusion. The pressure effect also has the expected direction, namely with the first addition of magnesium the pressure coefficient increases algebraically, which here means a numerical increase of

the positive coefficient. This is followed by a decrease at higher concentrations. The effect is small, but beyond experimental error. A precise evaluation of the significance of these results on the dilute solutions is obscured by the unknown effect of the impurity in the "100 per cent" lithium. This material is described by MacKay merely as "sodium free." Metals Handbook lists for the specific resistance at o°C of pure lithium 8.55 × 10<sup>-6</sup> against 9.17 found here. The temperature coefficient is not listed.

The resistances to 100,000 of the 20, 40, 60, and 80 compositions were in all cases smooth, with no suggestions of new phases. In order to secure agreement with the measurements in the 30,000 range the following corrections were applied to the changes of resistance between 20,000 and 100,000: for 20 Li an additive correction of 32 per cent; for 40 Li 13 per cent additive; for 60 Li agreement was perfect and no correction was applied; for 80 Li no adequate basis for comparison existed in the low pressure range because of the hysteresis, and the results given in the table are without correction. This means that for the 80 Li composition there is a break in the tangent at 30,000.

The compressions are given in Table VIII. Plotted against composition they lie smoothly and nearly linearly, except for 20 Li,

which lies slightly high.

The shearing curves show marked variations in character over the composition range. For 20 Li shearing strength at first rises with marked downward curvature to almost a horizontal asymptote, followed in the neighborhood of 50,000 by reversal and rapidly accelerated rise to a shearing strength of 2,000 kg/cm<sup>2</sup> at 80,000. This behavior is very similar to that of pure magnesium. The next two compositions, 40 and 60 Li, are both similar and normal in that shearing strength rises nearly linearly with pressure over the entire range, without hysteresis, to respective maxima of 8,400 and 5,700 kg/cm<sup>2</sup> at a pressure of 80,000. The 80 Li composition shows marked hysteresis. On the initial application shearing strength rises linearly with pressure to 600 kg/cm<sup>2</sup> at 40,000, where there is a cusp with sharp upward break in the tangent, the curve rising with rapid acceleration to a shearing strength of 2,600 at 80,000. On release of pressure there is hysteresis amounting at the maximum to 1000 kg/cm<sup>2</sup> on the shearing strength. The hysteresis loop is closed, with a break in the direction of the tangent, at

20,000. This behavior is qualitatively similar to that found a number of years ago for pure lithium, 10 which is the only other known example of this sort of behavior. It seems probable that we have here a polymorphic transition occurring only under the action of shearing stress. A similar transition is known<sup>11</sup> at atmospheric pressure at low temperature for pure lithium, and there is some

theory to account for it.

Lithium-Tin. According to Hansen this system is very complicated, there being six compounds which separate from the melt and seven alternating domains of mixed and homogeneous structure at lower temperatures. The region at room temperature between o and 20 atomic per cent tin is, according to Hansen, a mechanical mixture of Li and Li<sub>4</sub>Sn. No attempt was made here to make a complete investigation of the entire system; one reason for this was that Ufford 12 has already investigated the pressure effects up to 12,000 kg/cm<sup>2</sup> of six compositions. The domain up to 20 per cent tin is of special interest here in connection with the question of the effect of small additions to a metal with positive pressure coefficient of resistance. In this region Ufford had studied only the 9 and 10 per cent compositions. It seemed worth while to study more closely spaced compositions in this region, and accordingly alloys of 1, 2, 5, 10 and 20 per cent Mg were made. These were prepared in the regular way in closed iron containers. The 20 per cent composition, the compound Li<sub>4</sub>Mg, was found to be so brittle that nothing could be done with it. The 1, 2, and 5 compositions were soft enough to permit successful extrusion. Difficulty was encountered in extruding the 10 per cent composition, which spit out of the die in ragged gulps. This was, however, successfully formed into wire by squeezing in successively smaller collets in a jeweler's lathe. Resistance was measured to 30,000 in the regular way for these four compositions. In addition to these I had on hand a number of Ufford's compositions of 27 years ago, which had been kept sealed under nujol. Ufford had not attempted to measure the 80 Li-20 Sn composition, ostensibly the compound Li<sub>4</sub>Sn, saying that it was too brittle to handle. He had, however, succeeded in extruding a few short lengths, and with excessive caution Mr. Chase skillfully managed to get four spring clip leads attached to one of the pieces, and regular measurements to 30,000 were also made on this. In addition, another of Ufford's

compositions, 60 Li-40 Sn, was measured to 30,000 on the off chance of discovering something new in the new region between 12,000 and 30,000. Nothing new was found.

The results are shown in Table IX. Only electrical properties were measured for this series, and the effect of pressure on resistance only to 30,000. The most striking result is the approximate constancy of both temperature coefficient and pressure effect from pure lithium up to 10 per cent tin. This would seem to indicate

TABLE IX
LITHIUM-TIN SYSTEM

	100 Li	99 Li 1 Sn	98 Li 2 Sn	95 Li 5 Sn	90 Li 10 Sn	80 Li 20 Sn	60 Li 40 Sn
Density		.552	-555	.940	1.50	2.62	
ρ₀0 × 106	9.17	9.02	10.68	15.83	20.66	37.5*	20.9*
Temperature Coefficient	.00445	.00437	.00430	.00431	.00428		
Pressure kg/cm <sup>2</sup>			Rp/	Ro			
o	1.000	1.000	1.000	1.000	1.000	1.000*	1.000*
5,000	1.036	1.045	1.036	1.043	1.044	.945	.957
10,000	1.074	1.087	1.075	1.091	1.089	.900	.921
15,000	1.115	1.130	1.114	1.139	1.137	.861	.890
20,000	1.158	1.173	1.176	1.188	1.185	.829	.864
25,000	1.198	1.217	1.199	1.236	1.233	.800	.840
30,000	1.237	1.260	1.241	1.287	1.278	-773	.818.

<sup>\*</sup> Ufford's specimens. Specific resistance at room temperature.

very small solubility in pure lithium. On the average, the temperature coefficients of the alloys are slightly less than that of pure lithium, and the pressure coefficients, which are positive, somewhat higher. This is consistent with previous experience. The various minor irregularities in the progression of temperature and pressure coefficients may well be due to imperfect homogeneity in the material. Ufford measured in this range of composition only 9 and 10 per cent tin. His fractional changes of resistance at 10,000 were 0.088 and 0.084 respectively, to be compared with 0.089 found here.

It would appear that up to 10 per cent tin the system is almost entirely a mechanical mixture; if Hansen's diagram is right this would be a mechanical mixture of pure lithium with the compound Li<sub>4</sub>Sn. From the approximate constancy of the temperature and pressure coefficients the conclusion is to be drawn that the compound has nearly the same temperature and pressure coefficient as the pure metal. But this is completely inconsistent with present measurements on Ufford's specimen of the compound, which has a rather large negative pressure coefficient. The conclusion would seem to be forced that there is still another phase not known to Hansen between 10 and 20 per cent tin. This is also strongly suggested by Ufford's Figure 1, which demands a drastic break in the temperature and pressure coefficients in this range. Incidentally it is to be remarked that Ufford's value for the temperature coefficient of the 9 per cent composition, 0.00989, appears impossibly high. His temperature coefficients were not checked by a return reading, and he remarks that they were the least satisfactory of his measurements.

The composition 60 Li-40 Sn corresponds to the compound Li<sub>3</sub>Sn<sub>2</sub> shown by Hansen. The behavior of the resistance of this under pressure is not noteworthy, there being a fairly large negative pressure coefficient of resistance with curvature in the normal direction. My change of resistance of this composition at 10,000 is 0.079, against 0.068 by Ufford. This is far beyond either experimental error; it is to be noted that the specimens were not identical. Lead-Antimony. According to Hansen and Metals Handbook this system at room temperature consists of a simple eutectic mixture of nearly pure components, the mutual solubilities being one per cent or less. Five compositions were investigated in the following: 20, 40, 60, 80, and 99 atomic per cent antimony. Because of the large difference of melting point of the components the conditions were not specially favorable to homogeneity in the castings, and indeed appreciable differences of density were found between different parts of the same casting, rising in the extreme case to one unit in the first decimal place. The mean densities of the alloys were almost exactly a linear function of the composition, as would be expected of a eutectic.

All compositions were too brittle to form into wire by extruding and all resistance measurements, except on the 1 per cent lead composition, were made on specimens squeezed at 230°, the eutectic temperature being 252°. The 1 per cent lead was squeezed at 450°.

As a consequence of the unfavorable shape of the specimens the specific resistances are not accurate, but nevertheless should be significant. Specific resistance plotted against composition is far from smooth. With increasing lead content the specific resistance drops to an intermediate minimum at 40 Pb, rises to a secondary maximum at 60 Pb, and then drops sharply, being nearly the same at 80 and 100 Pb. This is definitely not the behavior to be expected of a eutectic. This behavior is confirmed by the temperature coefficient, which is not affected by error due to unfavorable shape of the specimen. The temperature coefficients of the first three compositions are lower than for pure metals, as would be expected of solutions of intermetallic compounds rather than of a eutectic mixture. The behavior of specific resistance may be complicated by lack of isotropy in the grains of pure antimony, but this can hardly be a factor in the behavior of temperature coefficient. Furthermore, there is a definite parallelism between the details of the variations of the specific resistance and the temperature coefficient, suggesting that the absolute error in the specific resistances is not important.

The resistances as a function of pressure are shown in Table X. Consider first the dilute composition 99 Sb-1 Pb. Resistance measurements to 30,000 only were made on two different specimens of this composition. Furthermore, only resistance measurements were made on this composition. The first specimen was prepared without special precaution, the weighed components being melted together in an evacuated quartz tube which was then quenched into water. The second specimen, after preparation as just described, was annealed in the quartz tube for 4 days at 600° and then quenched. During the annealing there was appreciable distillation of antimony to the upper part of the tube, so that the lead content of this specimen was doubtless somewhat in excess of one per cent. The effect of pressure on the resistance of both specimens was highly anomalous, with much hysteresis and permanent alteration of zero. The resistance of the first specimen decreased slightly on the initial application of pressure up to 10,000, from where it increased nearly linearly to about 10 per cent more than initial resistance at 30,000. On release of pressure, resistance was nearly stationary down to 15,000, where an accelerated increase began, ending at atmospheric pressure with a 25 per cent increase above

TABLE X
LEAD-ANTIMONY SYSTEM

	100 Pb	8o Pb	60 Pb	40 Pb	20 Pb	oo Pb	
	100 1 0	20 Sb	40 Sb	60 Sb	80 Sb	ı Sb	100 Sb
Density	11.33	10.43	9.39	8.46	7.52		6.96
$ ho_{00}  imes$ 10 $^6$	19.13	19	48	34	52	65.2	61.3
Temperatur Coefficient	.0042 I	.00368	.00224	.00296	.00241	\.00328* \.00398	.00466
Pressure kg/cm <sup>2</sup>				Rp	/Ro	( ),	
o	1.0000	1.000	1.000	1.000	1.000	1.000*	1.000
5,000	.9315	.937	.941	.938	.960	-977	
10,000	.8746	.885	.888	.882	.910	.964	1.060
15,000	.8245	.839	.839	.828	.860	.959	
20,000	.7817	.798	.793	.782	.814	.964	1.104
25,000	·7431	.759	-749	-737	.771	.977	
30,000	.7079	.723	.714	.697	.731	1.000	1.103
40,000	.651	.663	.647	.628	.662		1.078
50,000	.606	.609	.591	.569	.601		1.021
60,000	-573	.561	.544	.521	.551		.938
70,000	.546	.520	.504	.480	.511		.837
80,000	.524	.484	.469	.446	.478		.756
90,000	.505	.452	.433	.417	.444		.674
100,000	.490	.422	.398	.388	.415		.605
				$-\Delta$	V/Vo		
5,000	.0118	.0123	.0119	.0120	.0116		.0123
10,000	.0224	.0230	.0228	.0229	.O22I		.0235
15,000	.0323	.0333	.0330	.0329	.0319		.0343
20,000	.0414	.0427	.0422	.0420	.0410		.0441
25,000	.0499	.0512	.0511	.0503	.0494		.0533
30,000	.0579	.0586	.0593	.0579	.0572		.0620
35,000	.0650	.0660	.0670	.0651	.0646		.0698
40,000	.0718	.0730	.0740	.0716	.0714		.0768

\* See text

initial. On the first application of pressure to the second specimen there was an increase of resistance of 21 per cent in the first 5,000 kg/cm², followed by a further nearly linear increase to 1.54 times initial at 30,000. On first release, resistance decreased to a flat minimum near 12,000, followed by a small increase to 49 per cent more than initial. A second application of pressure was made to this specimen. The hysteresis was now much less and there was an approach to consistent behavior. With rising pressure there is a minimum of resistance near 12,000, followed by a rise to 30,000.

On second release the same minimum occurs, but with an exaggerated rise to a zero 10 per cent higher. The mean of second increase and decrease is a nearly symmetrical parabolic curve of resistance against pressure, with minimum at 15,000 at a resistance 4 per cent less than initial. This also is not far from the curve obtained with release of pressure on the first specimen. To a very rough approximation this may be assumed to be the probable final result for thoroughly seasoned material. The large initial changes are possibly an effect of shifting internal equilibrium. Metals Handbook remarks that at the lead rich end of the series equilibrium is attained at room temperature only over the course of years. The rough agreement of specific resistances and temperature coefficient for the two specimens of 1 per cent composition also suggests that the final values after exposure to pressure are perhaps not far from equilibrium values.

Taking these results on the 1 per cent Pb composition at their face value, an appreciable solubility of lead in antimony is indicated, the specific resistance of both specimens being higher than that of pure antimony, and the temperature coefficient of both lower. The effect of solute in dilute quantity on pressure effect on resistance is anomalous, however, the resistance of pure antimony at first increasing with increasing pressure and passing through a maximum, whereas that of the dilute solution at first decreases, passing through a minimum. It is to be kept in mind, however, that the complicating effects of non-isotropy, which is very marked in the resistance and the pressure coefficient of resistance of pure antimony, obscures the straightforward interpretation of the results.

The values of specific resistance and temperature coefficient listed in Table X for "100 Sb" require special comment. These are the values obtained on the MacKay antimony actually used in making these alloys, it being thought that this would be more significant than to give results for antimony of higher purity. The specific resistance and temperature coefficient were obtained on a specimen of this antimony squeezed at 400° C and measured by the four razor blade technique. The specific resistance and temperature coefficient differ notably from values which I have previously obtained  $^{13}$  on single crystal material of presumptively much higher purity. The specific resistance of that pure material was 33.6  $\times$  10-6 against 61.3 now, and the temperature coefficient 0.00510

against 0.00466 now. The resistance as a function of pressure given in Table X is from a recent publication <sup>14</sup> on the pure single crystal stock. The compressibility to 40,000 of the MacKay material was also freshly determined and is given in the table; the difference compared with previous <sup>15</sup> accurate values to 30,000 on

single crystal stock is of the order of 1 per cent.

Consider next the effect of pressure on the 20, 40, 60, 80 compositions. The resistance of these decreases from the start, with increasing pressure. There is no hysteresis or permanent change of resistance after release of pressure. Two of the compositions, 20 and 60 lead, show an initial episode in the first 5,000 kg/cm² of slight abnormal downward curvature, but in general, curvature is normal over the entire range. At the antimony rich end of the series the addition of 20 per cent lead results in an algebraic decrease of the pressure coefficient of resistance, an exception to the general rule shown also by the 99 Sb-1 Pb alloy. At the lead rich end the addition of antimony has the normal effect of increasing algebraically the pressure coefficient, that is, diminishing the proportional decrease of resistance produced by pressure.

The correction for making the readings to 100,000 agree with those to 30,000 is larger than usual and more consistent, varying from plus 40 to plus 55 per cent. It may be that the effects of shearing stress, which are an unavoidable accompaniment of the measurements to 100,000, are unusually large here and not adequately dealt with by a simple multiplicative correction. There is internal evidence of this from the resistance measurements themselves, because up to 30,000 the effect of pressure on resistance at the lead rich end of the series is greater on the alloys than on pure lead, whereas the relation reverses between 30,000 and 100,000. Further evidence in the same direction will appear from the shear-

ing measurements.

The compressions are shown also in Table X. The compressions of pure antimony and pure lead differ only slightly. On passing from antimony to lead in the series there is at first a small increase of compressibility, then a slight drop, and finally a slight increase

again to pure lead.

The shearing curves of all compositions show unusually large episodes. Pure antimony is known from compression measurements<sup>16</sup> to have a transition in the neighborhood of 80,000 kg/cm<sup>2</sup>.

There is no reflection of this in the shearing curve, which rises smoothly with upward curvature in this vicinity, but there is a definite episode in a point of inflection near 50,000. This point of inflection becomes much accentuated in the 80 Sb composition, the pressure of inflection now being 45,000. With the 60 Sb composition this inflection has developed into a well marked maximum and minimum, maximum at 40,000 and minimum at 53,000. With the 40 Sb composition the maximum and minimum with increasing pressure are smeared together into a point of inflection with horizontal tangent, but with decreasing pressure a small maximum and minimum appear at 40,000 and 50,000. With the 20 Sb composition the well marked maximum and minimum reappear, with very little hysteresis between increasing and decreasing pressure, at pressures of 40,000 and 55,000. The maximum shearing strengths at 80,000 of the six compositions, from pure antimony, through the four alloys, ending with pure lead are, respectively: 4,300, 3,000, 1,700, 3,200, 1,000, and 1,200. It would appear probable that we have here another example of some sort of a shearing transition, analogous to the shearing transition of lithium. Furthermore, since the progression of numerical values in the series is not regular, it would seem that the relations are not simple, with perhaps not continuous miscibility of the phases formed under shearing stress.

Lead-Tin. According to Hansen and also Metals Handbook the system at room temperature is a simple eutectic mixture of the practically pure components. There have been various claims of a transition at 150° in the solid phase on cooling and for a compound; neither of these claims seems well founded. The solubility of lead in tin is practically nil. Metals Handbook indicates a solubility of tin in lead of between one and two per cent. Pressure measurements were made here on four compositions, 25, 50, 75 atomic per cent lead and the dilute tin composition 99 Pb-1 Sn. In addition to the compositions measured under pressure, four other compositions, of 20, 40, 60, and 80 per cent were prepared and the densities determined at atmospheric pressure. These densities were 8.09, 9.07, 9.80 and 10.58 respectively with increasing lead content. The densities of these and the other compositions lie closely on a line joining the components, as would be expected of a mixture.

The resistance specimens for 30,000 were prepared by extrusion at room temperature. The data for compression and change of

TABLE XI LEAD-TIN SYSTEM

	100 Pb	99 Pb	75 Pb 25 Sn	50 Pb 50 Sn	25 Pb 75 Sn	100 Sn
Density	11.33	11.29	10.36	9.43	8.40	7.29
$\rho_{00} \times 10^{8}$	19.13	19.2	17.0	14.6	12.2	11.89
Temperature Coefficient	,00421	.00414	.00405	.00412	.00427	.00438
Pressure kg/cm <sup>2</sup>			Rp	Ro		
O	1.0000	1.000	1.000	1.000	1.000	1.0000
5,000	.9315	.933	.939	.944	.947	.9505
10,000	.8746	.876	.888	.896	.902	.9077
15,000	.8245	.826	.842	.854	.863	.8695
20,000	.7817	.783	.802	.816	.828	.8344
25,000	.7431	.745	.766	.783	.796	.8031
30,000	.7079	.710	.733	.752	.766	.7749
40,000	.651		.681	.702	-717	.724
50,000	.606		.638	.659	.677	.683
60,000	-573		.601	.624	.643	.647
70,000	.546		.571	.596	.612	.618
80,000	.524		.544	.570	.586	.592
90,000	.505		.522	-547	.562	.569
100,000	.490		.501	.523	.540	.548
			$-\Delta V$	Vo		
5,000	.0118		.0110	.0108	.0097	.0099
10,000	.0224		.0209	.0202	.0188	.0184
15,000	.0323		.0303	.0294	.0275	.0265
20,000	.0414		.0391	.0378	.0359	.0342
25,000	.0499		.0478	.0456	.0436	.0417
30,000	.0579		.0560	.0519	.0512	.0488
35,000	.0650		.0633	.0589	.0580	.0548
40,000	.0718		.0698	.0646	.0644	.0610

resistance are given in Table XI. Both are approximately smooth in pressure and lie between the values for the components, as would be expected of a mixture. The electrical parameters of the 99 Pb-1 Sn composition differ from those of pure lead in the direction to be expected of a solid solution (specific resistance higher, temperature coefficient lower, decrease of resistance under pressure numerically less), but the differences are very small and, except for specific resistance, about what might be expected in a mechanical mixture. The effect of any solution forces in this system would appear to be unusually small.

Although resistance and compression show no high pressure episodes, the shearing curves show a marked episode, varying consistently with composition. The composition 75 Pb-25 Sn shows a marked maximum shearing strength of 920 kg/cm<sup>2</sup> at a pressure of 50,000, followed by an equally sharp minimum of 710 at 75,000, followed by rise to 820 at 100,000. This curve was almost exactly retraced with decreasing pressure, which is somewhat unusual. The value 820 at 100,000 is probably a low record for shearing strength at this pressure. The composition 50-50 shows a horizontal point of inflection at 75,000 with increasing pressure, and with decreasing pressure a definite minimum of 920 at 70,000 and maximum of 980 at 55,000. The shearing strength at 100,000 of this composition was 1,300. The 25 Pb-75 Sn composition shows the same phenomenon in less degree, a horizontal point of inflection at 60,000 with shearing strength of 1,140 with increasing pressure, and with decreasing pressure at point of inflection, but without a horizontal tangent, in the same general vicinity. The shearing strength of this composition at 100,000 was 2,000, which lies on a regular progression with the two others. It would seem highly probable that this system experiences some sort of transition under shearing stress at high pressures which is not reflected in the behavior of resistance or of volume.

Lead-Zinc. According to Hansen and Metals Handbook the liquids in this system show only very partial solubility at both ends of the range and the solids are practically immiscible. The principal interest in a study of the pressure effects is to find whether any new phases or compounds are produced under pressure, and for this a

single composition, 50-50, is sufficient.

It would be expected that it would be difficult to prepare a homogeneous casting, and this indeed was the case. The mean density of the whole slug was 10.09 against 9.93 expected for a simple mechanical mixture, but extreme figures for the density of 9.53 and 11.16 were obtained from pieces from the top and bottom parts. This failure of homogeneity is not of importance considering that no new phases were found.

The resistance specimen for 30,000 was prepared by extrusion at room temperature. The numerical results for change of resistance and for compression are shown in Table XII. In general the alterations produced by pressure are between those for the components,

TABLE XII
LEAD-ZING SYSTEM

	100 Pb	50 Pb 50 Zn	100 Zn
Density	11.33	{10.09 11.16	7.08
$\rho_{00} \times 10^{6}$	19.13	17.8	5.5
Temperature Coefficient	.00421	.00410	.00408
Pressure kg/cm <sup>2</sup>		$R_{\mathbf{p}}/R_{0}$	
o	1.0000	1.000	1.000
5,000	.9315	.934	
10,000	.8746	.880	.937
15,000	.8245	.831	
20,000	.7817	.790	.887
25,000	.7431	-753	
30,000	.7079	.719	.847
40,000	.651	.665	.812
50,000	.606	.622	.783
60,000	.573	.587	.756
70,000	.546	.558	.733
80,000	.524	.532	.713
90,000	.505	.509	.695
100,000	.490	.487	.679
		$-\Delta V/Vo$	
5,000	.0118	.0103	.0079
10,000	.0224	.0199	.0157
15,000	.0323	.0289	.0229
20,000	.0414	.0372	.0297
25,000	.0499	.0452	.0362
30,000	.0579	.0529	.0424
35,000	.0650	.0600	.0484
40,000	.0718	.0664	.0541

which is about all that could be anticipated. In both cases the alterations are nearer to that for pure lead than would be expected from the nominal volume concentrations, but this probably is without significance.

The shearing curve, like the resistance and compression curves, is smooth and indicates no episode under pressure. The shearing curve is unusual in that it rises approximately linearly over the entire range, reaching a value of 1,600 kg/cm<sup>2</sup> at a pressure of 80,000.

Tin-Zinc. Hansen describes this system as a simple eutectic, with complete immiscibility of the two components in the solid phase. Metals Handbook leaves open the possibility of small solubility of zinc in tin. Measurements were made here on five compositions: 20, 40, 50, 60, and 80 atomic per cent tin. The castings were probably not as homogeneous as they should have been, the curve of density against composition departing from smoothness. In particular, the 50-50 slug would seem to have been more inhomogeneous than the others, as shown by a variation of density from 7.06 (top) to 7.16 (whole). Probably imperfect evacuation of the tubes in which the castings were made was partly responsible, there being definite evidence of oxidation. Contrasted with the density, the curve of specific resistance against composition is smooth, except for a slight deviation at the 50-50 point. The difference in behavior of density and resistance is in part due to the greater difference in specific resistance of the two components, one of which is more than twice that of the other, whereas the densities of the components differ by only 3 per cent, so that any irregularities are magnified.

The changes of resistance and compressions are given in Table XIII. The resistance specimens for 30,000 were made by extrusion at probably 150°. In general the changes of resistance and the compressions of the alloys are intermediate between those of the components, but the curves, when plotted against composition at a fixed pressure, are not particularly smooth. This is partly due to experimental error, the two components not differing greatly, and partly perhaps from uncertainty in the composition. It is also to be considered that neither of the pure components is isotropic; in particular the compressibility of zinc may vary eight fold with orientation and its pressure coefficient of resistance by a factor of two.17 Any preferential orientation of the grains of different compositions might obviously play an important part in lack of smoothness of the curves. The general result is that there is no evidence of any new phase at high pressure from the volume and resistance measurements. Neither is there any evidence for appreciable solubility at room temperature.

The shearing measurements also give no evidence for any new high pressure phase, although there are changes in the direction of curvature with pressure. The compositions 20, 40 and 60 Sn, and

TABLE XIII
Tin-Zing System

	100 Sn	80 Sn 20 Zn	60 Sn 40 Zn	50 Sn 50 Zn	40 Sn 60 Zn	20 Sn 80 Zn	100 Zn
Density	7.29	7.27	7.16	7.11	7.18	7.11	7.08
P00 × 106	11.89	10.59	9.13	8.68	7.72	6.66	5.5
Temperature Coefficient	.00438	.00420	.00418	.00416	.00414	.00406	.00408
Pressure kg/cm <sup>2</sup>				Rp/Ro			
o	0000.1	1.000	1.000	1.000	1.000	1.000	1.000
5,000	.9505	.956	.951	.961	.964	.968	
10,000	.9077	.916	.924	.928	.932	.941	.937
15,000	.8695	.881	.893	.897	.904	.916	
20,000	.8344	.849	.865	.871	.878	.894	.887
25,000	.8031	.820	.839	.845	.855	.874	
30,000	.7749	.794	.816	.824	.834	.856	.847
40,000	.724	.748	.776	.788	.796	.826	.812
50,000	.683	.708	.741	.758	.764	.802	.783
60,000	.647	.673	.713	-735	.744	.782	.756
70,000	.618	.645	.687	.714	.712	.766	.733
80,000	.592	.618	.666	.696	.693	.752	.713
90,000	.569	.594	.649	.680	.676	.742	.695
100,000	.548	.572	.632	.667	.661	-733	.679
			-	ΔV/Vo			
5,000	.0099	.0101	.0094	.0094	.0097	.0089	.0079
10,000	.0184	.0188	.0181	.0175	.0184	.0167	.0157
15,000	.0265	.0267	.0259	.0254	.0262	.0244	.0229
20,000	.0342	.0343	.0335	.0331	.0336	.0315	.0297
25,000	.0417	.0417	.0409	.0403	.0405	.0388	.0362
30,000	.0488	.0489	.0477	.0470	.0471	.0456	.0424
35,000	.0548	.0555	.0537	.0536	.0538	.0522	.0484
40,000	.0610	.0617	.0596	.0599	.0596	.0584	.0541

to a lesser extent 80 Sn, all show a common pattern: at the lower pressures, upward curvature, reversing at the middle of the range, followed by another upturn at the end of the range toward 80,000. The 50-50 composition, on the other hand, showed normal downward curvature over the entire range, with little rise, perhaps foreshadowing a maximum, between 80,000 and 100,000. The absolute shearing strengths at 80,000 were respectively as follows: 3,600, 4,400, 4,800, 3,700, 3,600, 3,600, and 1,650 (seven compositions in order, beginning with pure zinc, the five present alloys in order,

and pure tin). Notice that the shearing strengths of the alloys are greater than those of the components, instead of being intermediate, as were resistance and compression. This is to be expected, shearing slip not being additive from grain to grain, but one grain interferes with another. The pattern of changing curvature shown by the shearing curves, and not described in detail above, could perhaps be an effect of changing relative orientation of the grains.

# DISCUSSION AND SUMMARY

Only a few special points will be singled out for comment - in

general the numerical tables speak for themselves.

Perhaps the one most outstanding characteristic of the effect of pressure is the general absence of hysteresis or seasoning effects on the initial application of pressure. It would be natural to anticipate shifting internal equilibrium on change of pressure, with phenomena of creep and hysteresis. The fact that such were found so seldom indicates that for these metals at room temperature the solubility limits are little affected by pressure. The outstanding exception is alloys containing calcium. There is doubtless a correlation here with inadequate purity of the calcium, but in any event there would seem to be an effect of pressure on the solubility limits of the unknown impurity in the calcium.

The internal evidence offered by the resistance parameters suggests that in some cases the alloy system may be more complicated at room temperature than indicated by the diagrams in Hansen or in Metals Handbook. In the calcium-magnesium system the specific resistance shows no significant variation in the neighborhood of the supposed compound Ca<sub>3</sub>Mg<sub>4</sub>, although the shearing curves do have an episode at this composition. In the lithium-tin system it would seem that a compound of greater lithium content than Li<sub>4</sub>Sn is demanded. In the lead-antimony system the behavior of resistance is a more complicated function of composition than would be expected of the simple eutectic indicated by Hansen.

Two examples were found of small transitions induced by hydrostatic pressure. The alloy 14.3 Ca-85.7 Mg has a sluggish transition near 20,000 kg/cm² with abnormal direction of change of resistance, that is, the high pressure phase with smaller volume has the

higher resistance. The alloy 75 Cd-25 Sn shows a small discontinuity in resistance at 80,000, also in the abnormal direction.

Several examples were found of probable transitions induced by shearing stresses at high pressure which do not occur under the action of pure hydrostatic pressure. These transitions are in all cases reversible, but with possibly much hysteresis. The three cadmium-tin alloys, 25, 50, and 75 per cent, all show a shearing transition changing progressively in character with composition. 80 Li-20 Mg shows the same sort of transition, displaced toward higher pressures, as was previously found for pure lithium. It is probable that all the lead-antimony alloys have shearing transitions. The same is true of lead-tin alloys. It will appear in connection with other alloys of lead to be presented in later papers that it is not unlikely that pure lead has a shearing transition at pressures considerably in excess of 100,000, and that this transition can be brought down below 100,000 by the addition of an alloying element. The true significance of these shearing transitions is not at once evident without further data. It is to be recognized that we may have a true polymorphic transition (lattice change) produced by the hydrostatic pressure, the high pressure phase differing in its shearing constants from the low pressure phase, whereas the resistance and the volume parameters may differ by an imperceptible amount. Or we may have a second lattice which is stable only in cooperation with a fairly high shearing stress. Pure lithium and 80 Li-20 Mg are most probably of this latter type; the others are doubtful.

Finally, we have to consider the effect of the addition of small alloying elements on the pressure coefficient of resistance. In most cases the former generalization holds, namely that a small addition results in an algebraically greater pressure coefficient, whether the original coefficient is positive or negative. There are two apparent exceptions. In the calcium-cadmium system the exception is uncertain because of the unknown effect of impurity in the calcium. The significance of the apparent exception in the lead-antimony system is obscured by the very marked non-isotropy of antimony. Within the composition ranges studied here, of the order of a few per cent, the effect is not linear in composition, and it is evident that any characteristic effects of small additions on pressure coefficient play themselves out at very small concentrations. In the range studied here there is no indication of such an effect, for ex-

ample, as a characteristic modification of pressure coefficient for the addition of equal molecular concentrations of different alloying elements.

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